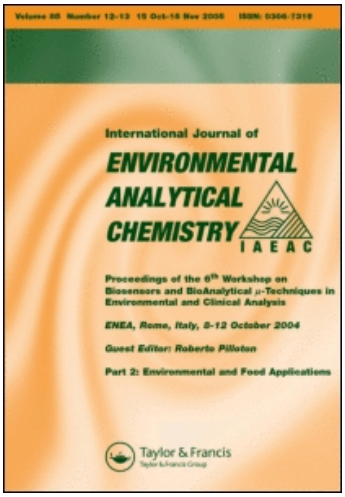

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Fujita, I.(1993) 'Determination of Sodium Linear Alkylbenzenesulfonate in River Water Containing Household Wastewater', International Journal of Environmental Analytical Chemistry, 50: 2, 83 — 89
To link to this Article: DOI: 10.1080/03067319308027587
URL: http://dx.doi.org/10.1080/03067319308027587

Intern. J. Environ. Anal. Chem., Vol. 50, pp. 83-89
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DETERMINATION OF SODIUM LINEAR ALKYLBENZENESULFONATE IN RIVER WATER CONTAINING HOUSEHOLD WASTEWATER

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(Received, 13 May 1992; in final form, 30 June 1992)

The effects of concomitant substances on colorimetric determination of sodium linear alkylbenzenesulfonate using Methylene Blue were studied with respect to proteins, food oil and starch, all considered to be components of household effluents. The determined values were compared with those obtained by high-performance liquid chromatography (HPLC). The quantitatively determined values were found to induce a negative error in the presence of proteins. This negative error was eliminated by the addition of propyl alcohol.

KEY WORDS : Anionic surfactants, colorimetric determination, HPLC, protein, river water.

INTRODUCTION

The total pollution load in river waters around populated cities is reportedly derived primarily from household wastewaters[1]. Although this situation is largely caused by delayed construction of basic social facilities (such as sewage disposal systems) to cope with the increasing population, quick solutions to perfect such facilities would be difficult in view of the present status of Japan. In assessing this issue, it is important to examine contamination from household effluents. Synthetic surfactants are substances that are widely used in homes and are not usually derived from natural components. Anionic surfactants are the main component of household detergents and have thus received attention from a number of researchers.

Sodium linear alkylbenzenesulfonate (LAS) are typical anionic surfactants. With recent advances and the spread of instrumental analysis, various methods for determining LAS in surface waters using high-performance liquid chromatography (HPLC) have been developed and applied[2]. We have already reported the determination of LAS by HPLC using a solid phase extraction by mini-cartridges[3]. On the other hand, a simple colorimetric method using Methylene Blue (Longwell-Abott method[4,5]) (JIS K0102[6]) is used for assessing the

level of contamination with surfactants (including LAS) in water areas on a governmental or citizen level. The compounds that are determined by this method are generally called Methylene Blue activated substances(MBAS). Differences between measurements by colorimetry and HPLC have been recognized from an analytical point of view. There have been many reports[7] of positive errors in colorimetric determination of substances except LAS, but little has been published on negative errors. This paper describes substances in household wastewater which cause negative errors, and present a method for diminishing them.

EXPERIMENTAL

Reagents and instruments

Absorption spectrochemical determination of the visible region was performed with a UVIDEC-610C (Nihon Bunko Co., Ltd.). The instrument used for HPLC was a Shimadzu LC4-A, and a LiChrospher RP-8 (5 μm, 250 × 4 mm I.D., Merck Co., Ltd.) was used as the packing column. The fluorometric detector was a Shimadzu RF-530. Methylene Blue, magnesium 8-aniline-1-naphthalenesulfonate (ANS) and propyl alcohol were obtained from WAKO Pure Chemical Industries (Osaka, Japan). Purified Neopelx F60® (Kao Atlas Co., Ltd.) was used as a standard of LAS.

Colorimetric determination with Methylene Blue

The colorimetric determination was conducted according to JIS K0102[6].

Determination by HPLC and concentration by SEP-PAK C_{18} minicartridge

The determination by HPLC using a solid phase extraction by SEP-PAK C_{18} minicartridge (Waters associates, Milford USA) was carried out according to previously described procedures[3].

Effects of concomitant substance on determination of LAS

Starch or food oil or protein (oviparous albumin) as concomitant substances were added to a standard solution of LAS (adjusted to 0.2 μg cm^{-3}). LAS was determined quantitatively after addition of each substance by both colorimetry and HPLC[3]. LAS after addition of various amounts of protein was also determined quantitatively by both colorimetry and HPLC[3].

Colorimetric determination by the addition of protein binding inhibitors

ANS or propyl alcohol as protein binding inhibitors were added to a protein LAS solution (adjusted to 5.0 and 0.2 μg cm^{-3}, respectively). LAS in protein solution after addition of protein binding inhibitors was also determined quantitatively by both colorimetry and HPLC[3].

RESULTS AND DISCUSSION

Quantitative determination of LAS containing concomitant organic substances by colorimetry and HPLC

Organic substances in household effluents are generally thought to be substances discharged from daily human activities, and are therefore considered to derive mainly from domestic fraction. For this reason, carbohydrates, fats and protein, which are all components of foods were studied. Standard LAS containing soluble starch, food oil for home use or protein was determined by colorimetry and HPLC[3] (Table 1). There was little difference in the values determined by colorimetry of HPLC[3] between the LAS with and without starch or food oil.

However, the presence or absence of proteins markedly influenced results between the two methods. Determination by HPLC after purification with a SEP-PAK C_{18} minicartridge revealed that the coefficient of variation (C.V.) of LAS concentration was less than 5.0%, indicating a sufficiently high accuracy of determination[3]. Quantification by HPLC showed no difference in values obtained in the presence or absence of protein.

Figure 1 shows the effect of protein on the determination of LAS by colorimetry and HPLC[3]. They suggest that the presence of protein, at least at a weight of about 5 times greater than that of LAS, affects the values obtained by colorimetry. The value of colorimetric determination with Methylene Blue in protein (5 μg cm^{-3}) standard solution was negligible. The hemolysis-inhibiting effect of surfactant is widely used in terms of the relationship between the agent and proteins. It has been reported that surfactants bind protein in serum, leading to a decrease in the effect[8]. The negative error observed in this study is considered to be due to inhibition of a complex formation with Methylene Blue as a result of the binding of surfactant to proteins.

Table 1 Effects of concomitant substances on the determination of LAS

	Colorimetry (μg cm^{-3}) *n=3*	*HPLC* (μg cm^{-3}) *n=3*
No addition		
Standard LAS solution	0.206±0.015	0.191±0.007
Addition		
Starch (1g dm^{-3})	0.183±0.024	0.188±0.007
Food oil (150 μg cm^{-3})	0.197±0.017	0.190±0.004
Protein (5 μg cm^{-3})	0.101±0.012	0.197±0.004

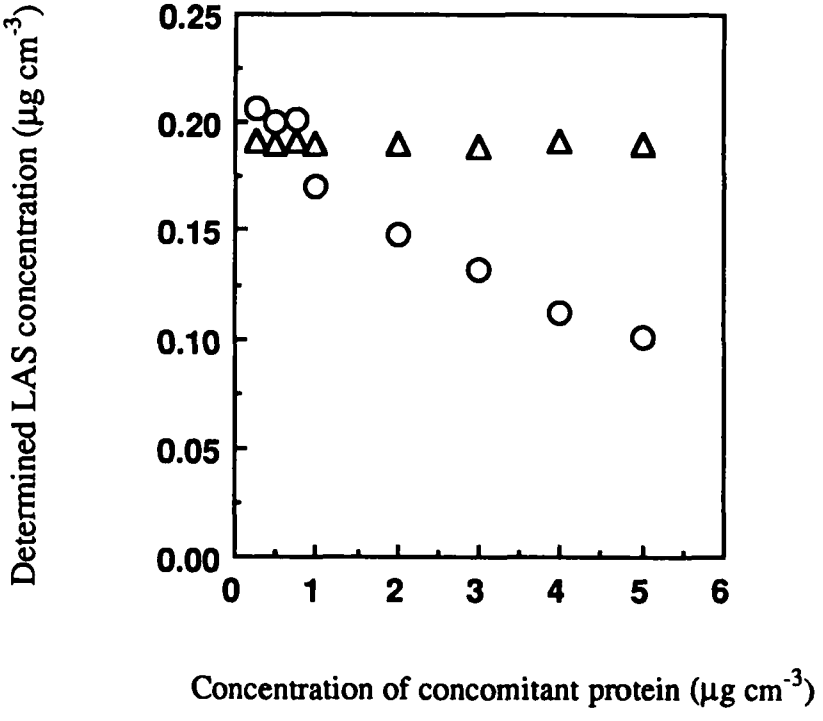

Figure 1 Effects of a concomitant protein on determination of LAS
O, Colorimetry; ; Δ, HPLC;

Determination of LAS in a protein LAS solution after addition of protein binding inhibitors by colorimetry and HPLC

The present experiment clarified the presence of protein causing a negative error in the determination of surfactant by colorimetry. To study the pattern of adsorption of LAS with the protein and identify a method for diminishing the negative error, the well-known protein binding inhibitors, ANS and propyl alcohol were added to a protein LAS solution to inhibit protein binding. Consequently, LAS was determined and the results are shown in Table 2. The addition of ANS yielded a higher value than that in protein-free LAS solution under the present experimental conditions. This suggests that ANS structurally resembles LAS and is likely to form a complex with Methylene Blue. ANS is considered to produce a positive error.

Propyl alcohol is generally known as a protein binding inhibitor and a protein denaturing agent, and was thus used in this experiment. When 20% of propyl alcohol was added, the colorimetric determination of the protein LAS solution gave a virtually equivalent value to that of the protein-free LAS solution. At the different concentrations of the protein LAS solution, as shown in Figure 1, protein binding was similarly prevented when 20% propyl alcohol was added, suggesting that LAS binds to the protein primarily based on hydrophobic interaction. The colorimetric determination of the protein-free LAS solution with 20% propyl alcohol gave an equivalent value to that of the protein-free LAS solution without propyl alcohol.

Table 2 Effects of protein binding inhibitors on the determination of protein-LAS mixed solution

	Colorimetry ($\mu g\ cm^{-3}$) *n=3*	*HPLC* ($\mu g\ cm^{-3}$) *n=3*
Protein-free LAS solution (blank)	0.206±0.015	0.191±0.007
Protein LAS solution (control)	0.101±0.012	0.197±0.004
Addition of ANS		
100($\mu g\ cm^{-3}$)	1.762±0.198	0.125±0.007
10($\mu g\ cm^{-3}$)	0.982±0.118	0.138±0.006
1($\mu g\ cm^{-3}$)	0.778±0.095	0.147±0.008
0.1($\mu g\ cm^{-3}$)	0.587±0.064	0.153±0.005
Addition of n-C_3H_7OH		
20%	0.201±0.029	0.188±0.009
10%	0.109±0.011	0.189±0.005
5%	0.115±0.013	0.195±0.003

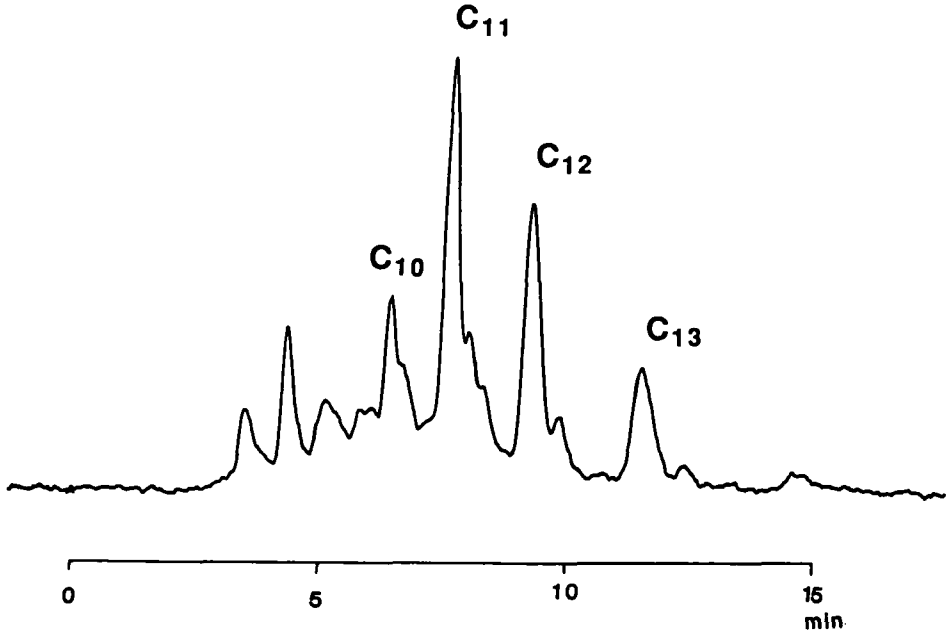

Figure 2 Chromatogram of LAS in protein LAS solution with ANS
Paking column: Lichrosher RP-8, 5 μm, 4 mm I.D × 250 mm
Eluant: 0.15 mol dm^{-3} $NaClO_4$ + H_2O (pH 2.3): CH_3CN=45:55,0.7 $cm^3\ min^{-1}$
Temperature; 52°C
Detected fluorescence wavelength : E_X225 nm, E_M 290nm

Table 3 Effects of a propyl alcohol on determination of LAS in river water

	Colorimetry ($\mu g\ cm^{-3}$) *n=3*	*HPLC* ($\mu g\ cm^{-3}$) *n=3*
River water A		
No addition (control)	1.101±0.024	1.291±0.009
Propyl alcohol (20%)	1.852±0.021	1.220±0.011
River water B		
No addition (control)	1.354±0.017	1.503±0.002
Propyl alcohol (20%)	1.951±0.031	1.498±0.008

The quantitative measurements by the HPLC method are incorporated here for comparison. Though a slight influence was found when ANS was used, virtually equal values were obtained (Figure 2). When the concentration of propyl alcohol was increased to 20% or higher, though protein binding was inhibited, the propyl alcohol influenced the solid phase adsorption and solvent extraction so that the recovery ratio was reduced.

Determination of LAS in contaminated river water by addition of a propyl alcohol

Propyl alcohol facilitated the release of the LAS bound to protein. By utilizing this effect, LAS in river water (Kengun river) from densely inhabited districts was quantitatively determined by colorimetry and HPLC in the presence of propyl alcohol. The results are shown in Table 3. Table 4 shows the water quality of the river waters. Values of N and P, which are generally called nutrient salts, were relatively high because the river water contained a large proportion of household effluent. The colorimetry values of river water

Table 4 Water quality of river water

	River water A *n=2*	*River water B* *n=2*
pH	7.3	7.4
DO($\mu g\ cm^{-3}$)	2.4	4.6
BOD($\mu g\ cm^{-3}$)	23.6	29.8
COD($\mu g\ cm^{-3}$)	33.3	28.9
SS($\mu g\ cm^{-3}$)	10	12
NH_4-N($\mu g\ cm^{-3}$)	2.29	1.33
NO_2-N($\mu g\ cm^{-3}$)	0.67	0.42
NO_3-N($\mu g\ cm^{-3}$)	0.11	0.85
PO_4-P($\mu g\ cm^{-3}$)	1.12	1.71
T-N($\mu g\ cm^{-3}$)	9.79	10.90
T-P($\mu g\ cm^{-3}$)	1.98	1.98
Cl($\mu g\ cm^{-3}$)	33.0	45.7

DO: dissolved oxygen; BOD: biochemical oxygen demand; COD: chemical oxygen demand; SS: suspended substance; NH4-N: ammonium nitrogen; NO_2-N: nitrite nitrogen; NO_3-N: nitrate nitrogen; PO_4-P: phosphate phosphorous; T-N: total nitrogen; T-P: total phosphorous

samples are usually higher than those of HPLC[9]. The addition of propyl alcohol to river water samples induced usual relationship between the values obtained by colorimetry and those obtained by HPLC. The present results also suggest that determination after exclusion of the effects of highly adsorptive substances is necessary in actual river water in which some protein-like hydrophobic substances having properties of high adsorption are considered to be present.

Acknowledgment

We express our thanks to Dr. Taishi Oda, for his co-operation in this study.

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